Use of a Solvatochromic Probe for Study of Solvation in Ternary Solvent Mixture

Narayan Ray and Sanjib Bagchi*

Department of Chemistry, Burdwan University, Burdwan-713 104, India

Received: September 23, 2004; In Final Form: October 18, 2004

Solvation characteristics of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino)phenolate in completely miscible ternary solvent mixtures (viz., methanol + acetone + water, methanol + acetone + benzene, and methanol + chloroform + benzene) have been studied by using an electronic spectroscopic procedure. The transition energy (E) corresponding to the charge-transfer band maximum of the solute in a ternary solvent mixture differs significantly from the average E-values in the component solvents weighted by the mole fraction of the solvents. A two-phase model of solvation has been invoked to explain the results. The excess or deficit of solvent components in the local region of the solute molecule over that in the bulk has been estimated using the knowledge of solvation in binary solvent mixtures.

Introduction

The study of solvation in terms of solute−solvent and solvent−solvent interactions is an important area of solution chemistry. While the latter interaction is constant in a pure solvent, the use of mixed solvent provides a means of its modification by varying the composition of the solvent mixture. As such, the chemical physics of solvation in solvent mixtures is a subject of current interest.[1−8] Experimental evidence suggests that the solute may induce a change in the composition of the solvation sphere compared to that in the bulk.[9] The phenomenon, known as preferential solvation, has been studied in recent years for binary solvent mixtures, both experimentally[10−16] and theoretically,[17−21] in terms of solvent−solvent and differential solute−solvent interactions. Addition of a third solvent component is likely to modify the solvent−solvent interaction in the immediate neighborhood of the solute. Systematic investigation along these lines has not yet been made. It is therefore instructive to study the modification of the local composition compared to that in the bulk as induced by the interactions in a ternary solvent mixture.

Electronic spectroscopy provides a suitable method for studying solvation interaction. It has been observed that the maximum energy (E) of absorption at the charge-transfer (CT) transition in various solutes acts as a reporter of the local composition around the solute molecule and reflects the solute−solvent and solvent−solvent interactions at the microscopic level.[22] It has been known that the value of E for the dye 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino)phenolate in a given solvent (often known as the $E_T(30)$ value of the solvent) depends dramatically on the solvent.[23,24] In a series of communications, it has been shown that information about the local composition is often obtained in a binary solvent mixture by studying the $E_T(30)$ values.[24] In recent communications, we have also reported preliminary investigations on the solvation of this dye in ternary solvent mixtures.[25,26] The objective of this paper is to study the role of solute−solvent and solvent−solvent interactions on the solvation characteristics of the dye as obtained by monitoring the $E_T(30)$ values as a function of solvent composition in ternary solvent mixtures. Three solvent mixtures, namely, methanol + acetone + water, methanol + acetone + benzene, and methanol + chloroform + benzene, have been included in the present study. The solvation characteristics of the solute in binary solvent mixtures containing these solvents have been reported in the literature.[10,35] A realistic model of solvation in a ternary solvent mixture has been presented to interpret the results. Information about the knowledge of binary solvation involving the solvents as obtained from the literature has been utilized to analyze the results on ternary solvation using the model.

Experimental Section

A sample of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino)phenolate, the indicator solute for the $E_T(30)$ scale, was obtained from Professor Ch. Reichardt, Marburg, Germany, as a gift. Methanol, ethanol, acetone, benzene, and chloroform were purified and dried by standard procedures.[27] All of the solvents were distilled from calcium hydride immediately prior to experiment. This ensured the absence of oxidizing impurities in the solvent. Triply distilled water was used for the experiments. Mixed solvents were prepared by carefully mixing the components by weight. Special care was taken to avoid contamination by air/moisture during mixing of the solvent components. Spectral measurements were taken on a Shimadzu UV2101PC spectrophotometer. Temperature was controlled to 298 ± 0.1 K by circulating water from a thermostat. Band maximum was determined by using the peak-finding software on the instrument. To check the reproducibility, the position of the band maximum in a particular solvent mixture was measured in a number of replicate measurements. The precision of replicate measurement was ±1 nm. Concentrations of the solute in the solutions were in the range 10^{-4}−10^{-5} M. The E-value was calculated from the wavelength maximum according to the following formula

$$E/\text{kcal mol}^{-1} = 28\,590/(\lambda/\text{nm}) \qquad (1)$$

The inaccuracy of ±1 nm in the measurement of λ leads to inaccuracy in the value of the energy maximum of ±0.1 kcal mol^{-1}.

Results

The CT absorption band of the solute in the ternary mixture appears broad and structureless. Solvatochromism of the band

---

* E-mail: bsanjibb@yahoo.com.

10.1021/jp0456741 CCC: $30.25

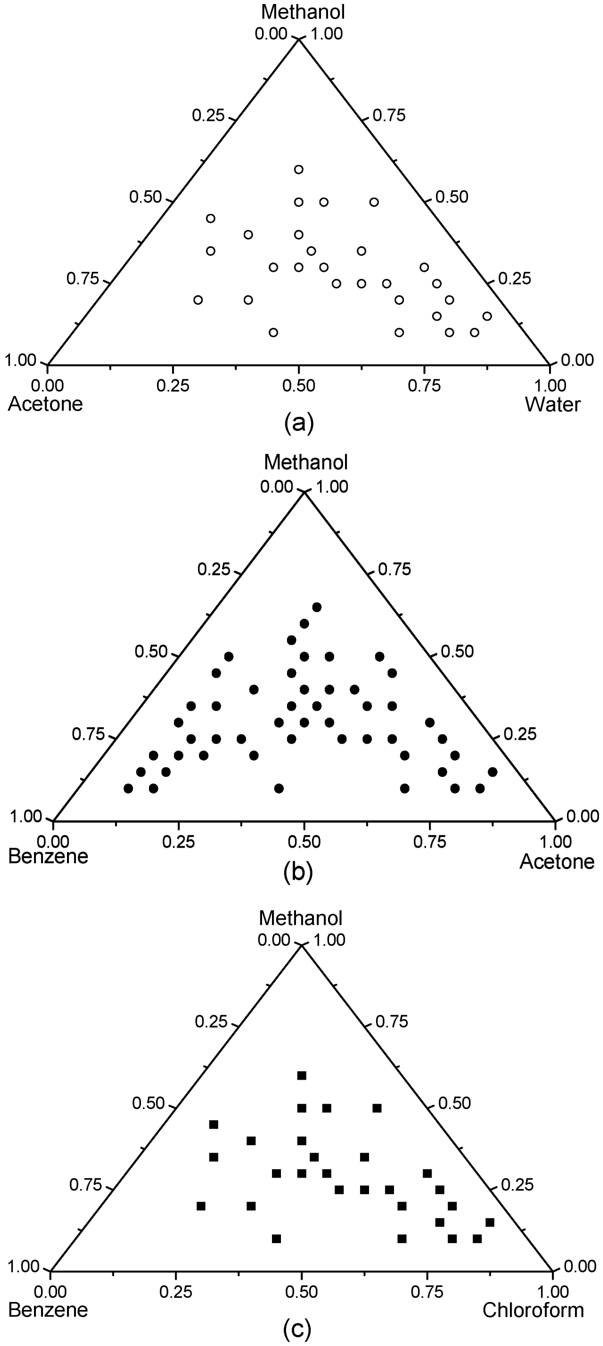


Figure 1. Composition of ternary mixtures used in the present study: (a) = methanol + acetone + water; (b) = methanol + acetone + benzene; (c) = methanol + chloroform + benzene.

TABLE 1: The Energy of Band Maximum (E_{123}) and Other Related Parameters as a Function of Solvent Composition of the Ternary Solvent Mixture Water (1) + Methanol (2) + Acetone (3) at 298 K for Betaine Dye

x_1	x_2	E^a	$E_{id}{}^a$	Δ^a	δ_1	δ_2	δ_3
0.20	0.20	52.4	57.6	−5.2	−0.31	0.09	0.22
0.60	0.20	51.1	49.2	1.9	−0.07	0.25	−0.18
0.30	0.30	51.9	54.8	−2.9	−0.23	0.14	0.09
0.40	0.30	51.3	52.7	−1.4	−0.17	0.16	0.01
0.25	0.50	53.1	54.5	−1.4	−0.16	0.15	0.01
0.50	0.25	50.7	50.9	−0.2	−0.13	0.18	−0.05
0.30	0.20	50.9	55.5	−4.6	−0.28	0.09	0.19
0.30	0.40	52.6	54.1	−1.5	−0.18	0.16	0.02
0.10	0.45	53.6	57.9	−4.3	−0.28	0.11	0.17
0.35	0.35	51.6	53.4	−1.8	−0.18	0.14	0.04
0.45	0.35	52.4	51.3	1.1	−0.11	0.25	−0.14
0.45	0.25	51.0	52.0	−1.0	−0.15	0.16	−0.01
0.35	0.30	51.6	53.8	−2.2	−0.19	0.13	0.06
0.15	0.35	52.9	57.6	−4.7	−0.30	0.12	0.18
0.55	0.25	50.8	49.9	0.9	−0.09	0.21	−0.12
0.60	0.30	50.3	48.5	1.8	−0.05	0.21	−0.16
0.65	0.25	50.2	47.8	2.4	−0.05	0.25	−0.20
0.65	0.10	49.6	48.8	0.8	−0.06	0.15	−0.09
0.70	0.15	49.3	47.5	1.8	−0.05	0.22	−0.17
0.70	0.20	49.9	47.1	2.8	−0.04	0.27	−0.23
0.75	0.10	48.3	46.8	1.5	−0.03	0.16	−0.13
0.80	0.10	48.3	45.7	2.6	−0.01	0.21	−0.20
0.80	0.15	48.9	45.4	3.5	−0.01	0.28	−0.27
0.20	0.40	52.9	56.2	−3.3	−0.25	0.13	0.12
0.20	0.60	52.9	54.8	−1.9	−0.14	0.07	0.07
0.30	0.50	52.3	53.4	−1.1	−0.13	0.11	0.02
0.40	0.10	51.3	54.1	−2.8	−0.18	0.07	0.11
0.40	0.50	52.4	51.3	1.1	−0.06	0.17	−0.11

[a] In kcal mol^{-1}.

is continuous, reversible, and independent of the concentration of the solute in the range studied. The bandwidth and shape practically remain unchanged, and no isosbestic point is observed in the spectrum. All these facts indicate that the shift of band maximum is not caused by a change of equilibria between different chemical species in solution. Figure 1 shows the experimental solvent compositions on a triangular plot. Values of maximum absorption energy in a ternary solvent mixture, E_{123}, at various compositions at 298 K have been listed in Tables 1−3. For an ideal solvation behavior, the value of a solvent-sensitive property of a solute in a mixed solvent is supposed to be given by the mole fraction average of the property in pure component solvents.[18,28] Thus, in an ideal case, the value of the maximum energy of absorption in a ternary mixture will be as follows

$$E_{123}(\text{ideal}) = x_1E_1 + x_2E_2 + x_3E_3 \qquad (2)$$

E_i and x_i in eq 3 represent the maximum energy of absorption and mole fraction of ith solvent, respectively. Values of E_{123}(ideal) and its difference from E_{123}, Δ, have been listed in Tables 1−3. Note that a significant deviation of E_{123} from the ideal value has been observed. While the deviation from the ideal value is always positive for the mixtures methanol + acetone + benzene and methanol + chloroform + benzene, both positive and negative deviations have been observed in the case of methanol + acetone + water system. In our earlier work,[25,26] we used the following equation to represent the composition dependence of the solute property, E_{123}, in a ternary solvent mixture

$$E_{123} = E_{123}(\text{ideal}) + x_1x_2x_3(A + Bx_1 + Cx_2) \qquad (3)$$

where A, B, and C are constants for a particular ternary mixture. It may be mentioned that similar expressions have been used previously to describe the composition dependence of a property in a ternary solvent mixture in the absence of any solute.[29−33] In the present case, also, eq 3 represents the experimental data points with the best-fit values of the coefficients A, B, and C (within an uncertainty limit of ca. 10%) as given in Table 4. Figure 2 shows the computed iso-Δ lines for the ternary systems. It appears that iso-Δ lines are closed curves. The area enclosed by the curve decreases as the value of Δ increases. It appears that similar plots are obtained for methanol + acetone + benzene and methanol + chloroform + benzene systems. The estimated solvent composition (x_{methanol}, x_{benzene}) where the deviation from ideality is maximum can be estimated as (0.2, 0.3) and (0.2, 0.5), respectively, for methanol + acetone + benzene and methanol + chloroform + benzene mixture. For methanol + acetone + water, however, the nature of iso-Δ plot

TABLE 2: The Energy of Band Maximum (E_{123}) and Other Related Parameters as a Function of Solvent Composition of the Ternary Solvent Mixture Methanol (1) + Acetone (2) + Benzene (3) at 298 K for Betaine Dye

x_1	x_2	E^a	$E_{id}{}^a$	Δ^a	δ_1	δ_2
0.20	0.20	47.6	40.4	7.2	0.38	−0.15
0.20	0.60	48.6	43.5	5.1	0.35	−0.32
0.30	0.30	48.8	43.4	5.4	0.33	−0.21
0.30	0.40	49.4	44.1	5.3	0.34	−0.27
0.50	0.25	50.5	47.3	3.2	0.20	−0.16
0.25	0.50	48.8	43.8	5.0	0.33	−0.29
0.20	0.30	47.4	41.2	6.2	0.36	−0.22
0.40	0.30	51.0	45.5	5.5	0.33	−0.22
0.45	0.10	51.0	45.1	5.9	0.30	−0.08
0.35	0.35	49.6	44.8	4.8	0.30	−0.24
0.35	0.45	50.1	45.6	4.5	0.30	−0.27
0.25	0.45	48.3	43.4	4.9	0.32	−0.28
0.30	0.35	48.9	43.7	5.2	0.32	−0.24
0.35	0.15	48.7	43.3	5.4	0.28	−0.11
0.25	0.55	48.9	44.2	4.7	0.32	−0.29
0.30	0.60	49.7	45.7	4.0	0.28	−0.26
0.25	0.65	49.6	44.9	4.7	0.32	−0.29
0.10	0.65	46.0	41.7	4.3	0.31	−0.31
0.15	0.70	48.2	43.2	5.0	0.34	−0.32
0.20	0.70	48.5	44.3	4.2	0.29	−0.27
0.10	0.75	46.6	42.5	4.1	0.28	−0.28
0.10	0.80	46.3	42.8	3.5	0.24	−0.23
0.15	0.80	47.6	43.9	3.7	0.36	−0.32
0.40	0.20	49.0	44.7	4.3	0.24	−0.14
0.60	0.20	49.9	49.1	0.8	0.07	−0.10
0.50	0.30	50.3	47.7	2.6	0.17	−0.17
0.10	0.40	45.4	39.7	5.7	0.35	−0.26
0.50	0.40	51.3	48.5	2.8	0.19	−0.18
0.25	0.25	48.1	41.9	6.2	0.35	−0.18
0.25	0.35	48.4	42.6	5.8	0.35	−0.24
0.45	0.45	50.8	47.8	3.0	0.21	−0.19
0.35	0.10	48.4	42.9	5.5	0.10	−0.08
0.15	0.15	46.6	38.9	7.7	0.39	−0.12
0.25	0.20	48.0	41.5	6.5	0.35	−0.15
0.20	0.15	47.4	40.0	7.4	0.38	−0.12
0.30	0.10	48.0	41.8	6.2	0.31	−0.08
0.10	0.15	45.4	37.8	7.6	0.38	−0.11
0.40	0.40	50.2	46.3	3.9	0.26	−0.23
0.55	0.20	50.6	48.0	2.6	0.16	−0.13
0.50	0.10	49.5	46.2	3.3	0.18	−0.07
0.35	0.50	50.1	45.9	4.2	0.28	−0.26
0.35	0.30	49.1	44.4	4.7	0.28	−0.20
0.25	0.15	47.7	41.1	6.6	0.34	−0.12
0.10	0.10	45.0	37.5	7.5	0.37	−0.08
0.20	0.10	46.4	39.6	6.8	0.34	−0.08
0.45	0.25	49.8	46.2	3.6	0.22	−0.17
0.65	0.20	51.1	50.2	0.9	0.12	−0.10
0.15	0.10	46.1	38.5	7.6	0.37	−0.08
0.40	0.35	49.7	45.9	3.8	0.25	−0.22

[a] In kcal mol^{-1}.

TABLE 3: The Energy of Band Maximum (E_{123}) and Other Related Parameters as a Function of Solvent Composition of the Ternary Solvent Mixture Methanol (1) + Chloroform (2) + Benzene (3) at 298 K for Betaine Dye

x_1	x_2	E^a	$E_{id}{}^a$	Δ^a	δ_1	δ_2
0.20	0.20	47.65	39.78	7.87	0.40	0.21
0.20	0.60	47.45	41.62	5.83	0.26	0.29
0.30	0.30	48.70	42.42	6.28	0.33	0.13
0.30	0.40	48.62	42.88	5.74	0.29	0.16
0.50	0.25	50.12	46.55	3.57	0.19	0.07
0.25	0.50	47.89	42.25	5.64	0.27	0.22
0.20	0.30	47.65	40.24	7.41	0.36	0.26
0.40	0.30	49.45	44.60	4.85	0.26	0.08
0.45	0.10	49.92	44.77	5.15	0.28	0.07
0.35	0.35	48.83	43.74	5.09	0.27	0.09
0.35	0.45	48.88	44.20	4.68	0.24	0.12
0.25	0.45	47.97	42.02	5.95	0.29	0.21
0.30	0.35	48.51	42.65	5.86	0.30	0.15
0.35	0.15	49.16	42.82	6.34	0.34	0.11
0.25	0.55	47.87	42.48	5.39	0.26	0.20
0.30	0.60	48.41	43.80	4.61	0.23	0.14
0.25	0.65	47.57	42.94	4.63	0.22	0.19
0.10	0.65	45.67	39.67	6.00	0.21	0.52
0.15	0.70	47.10	40.99	6.11	0.25	0.39
0.20	0.70	47.14	42.08	5.06	0.22	0.28
0.10	0.75	45.45	40.13	5.32	0.18	0.48
0.10	0.80	45.89	40.36	5.53	0.18	0.53
0.15	0.80	46.68	41.45	5.23	0.20	0.39
0.40	0.20	49.64	44.14	5.50	0.29	0.11
0.60	0.20	50.92	48.50	2.42	0.13	0.04
0.50	0.30	50.16	46.78	3.38	0.18	0.06
0.10	0.40	45.93	38.52	7.41	0.30	0.49
0.50	0.40	49.94	47.24	2.70	0.15	0.03

[a] In kcal mol^{-1}.

TABLE 4: Values of *A*, *B*, and *C* for Different Ternary Solvent Mixtures

solvent mixture	A	B	C
acetone + methanol + water	−519	914	445
acetone + methanol + benzene	656	−295	992
chloroform + methanol + benzene	279	326	−540

is different. In this case, two regions are clearly distinguished. The water-rich region (N) is characterized by a negative value of Δ, while for the acetone-rich region (P), the value of Δ is positive (Figure 2a). The changeover from the negative to the positive value of Δ takes place when $x_{\text{acetone}}/x_{\text{water}}$ exceeds 1.5.

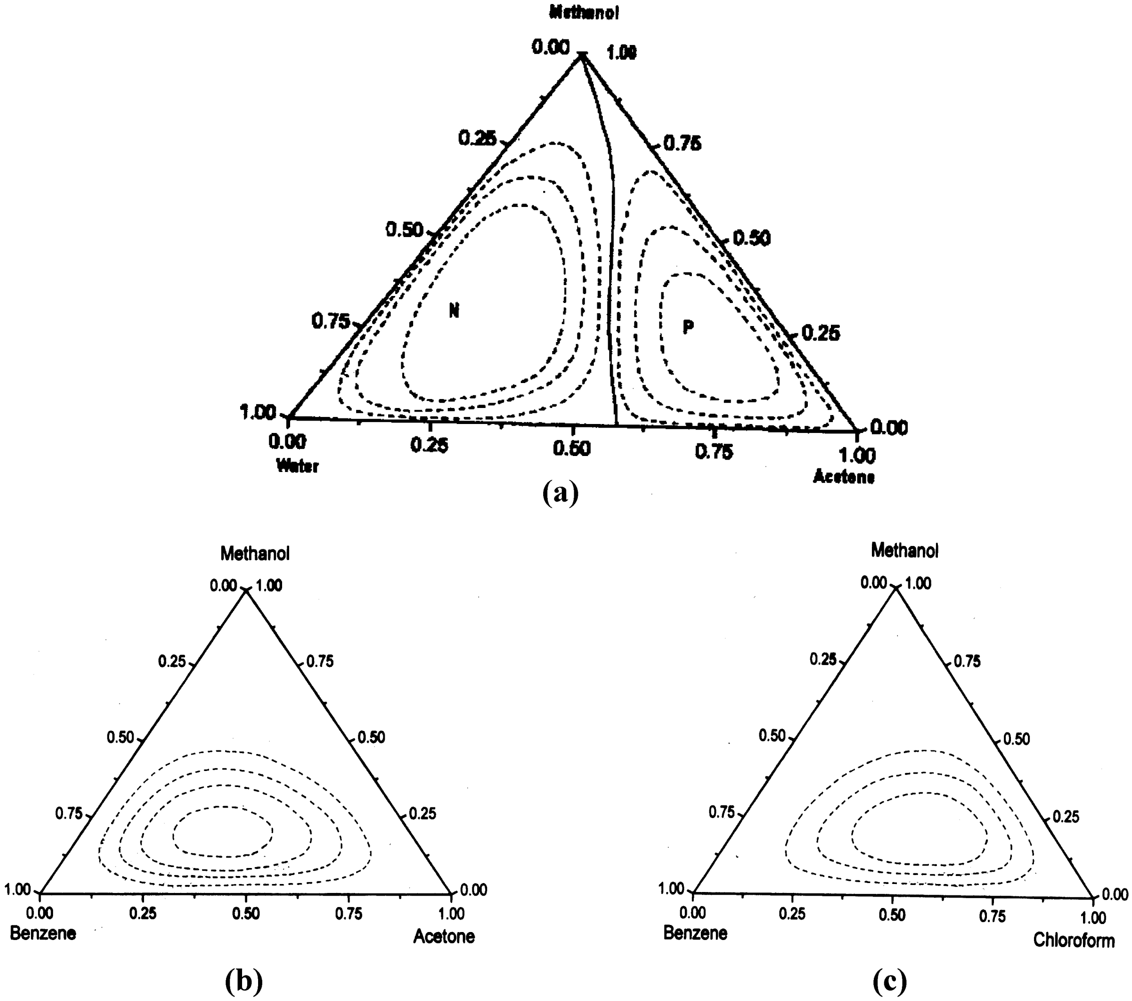
Discussion

It is known that the solute interacts with the solvents through nonspecific and specific modes of solvation interaction, and the maximum absorption energy depends on the dipolarity and acidity of the solvent.[24,34] Thus, in a ternary solvent mixture, the solute will be solvated by the three component solvent molecules; the relative extent of interaction will, however, depend on the composition. To describe solvation in a ternary solvent mixture, we use the following model, which is an extension of the existing two-phase model of solvation in a binary solvent mixture where solvent molecules presumably distribute between the local and the bulk phases.[21] The equilibrium distribution of the solvent molecules between the local and the bulk phases will be determined by the criterion of minimum Gibbs free energy (G) of the solute−solvent system. If N_i^{L} and N_i are the number of solvent molecules of ith type in the local and the bulk regions, respectively, the G for the system is given by the following expression

$$\begin{aligned}G = {} & [N_1^{\text{L}}\epsilon_{s1}^{\text{L}} + N_2^{\text{L}}\epsilon_{s2}^{\text{L}} + N_3^{\text{L}}\epsilon_{s3}^{\text{L}}] + [N_1^{\text{L}}(N_1^{\text{L}} - 1)\epsilon_{11}^{\text{L}}/2 + \\ & N_2^{\text{L}}(N_2^{\text{L}} - 1)\epsilon_{22}^{\text{L}}/2 + N_3^{\text{L}}(N_3^{\text{L}} - 1)\epsilon_{33}^{\text{L}}/2 + N_1^{\text{L}}N_2^{\text{L}}\epsilon_{12}^{\text{L}} + \\ & N_3^{\text{L}}N_2^{\text{L}}\epsilon_{23}^{\text{L}} + N_1^{\text{L}}N_3^{\text{L}}\epsilon_{31}^{\text{L}}] + [N_1(N_1 - 1)\epsilon_{11}/2 + N_2(N_2 - \\ & 1)\epsilon_{22}/2 + N_3(N_3 - 1)\epsilon_{33}/2\,] + N_1N_2\epsilon_{12} + N_2N_3\epsilon_{23} + \\ & N_3N_1\epsilon_{13} - \{kT\ln[(N_1^{\text{L}} + N_2^{\text{L}} + N_3^{\text{L}})!/(N_1^{\text{L}}!N_2^{\text{L}}!N_3^{\text{L}}!)] + \\ & kT\ln[(N_1 + N_2 + N_3)!/(N_1!N_2!N_3!)]\} \quad (4)\end{aligned}$$

In eq 4, ϵ_{si} and ϵ_{sj} are the energies of solute − i-solvent and i-solvent − j-solvent interactions. The superscript L indicates the local phase. The first term in the square bracket on the right-hand side of eq 4 represents solute−solvent interaction, the second and third terms in brackets represent solvent−solvent interaction in the local and bulk regions, respectively. The fourth term represents the entropy term. N_i^{L} and N_i are related by particle number conservation as follows

$$N_i^{\text{L}} + N_i = N_i^{\text{T}} = \text{total number of } i\text{-solvent molecules } (i = 1, 2, 3) \quad (5)$$



(a)

(b)

(c)

Figure 2. Curves of constant Δ-value for water + methanol + acetone (a), methanol + acetone + benzene (b), and methanol + chloroform + benzene (c). Δ-values in kcal mol^{-1} for iso-Δ curves (from outermost to innermost) are 4.0, 6.0, 8.0, and 10.0, respectively, for (b) and 4.0, 6.0, and 8.0, respectively, for (c). For (a), the positive and negative Δ-values are shown in the regions P (Δ = 1.0, 2.0, and 3.0 from outer to inner) and N (Δ = −0.5, −1.0, and 2.0, respectively). Compositions on the solid curve are characterized by Δ = 0.

Values of N_1^L, N_2^L, and N_3^L vary with solvent composition. We assume that the total number of molecules in the local region (cybotactic zone), $(N_1^L + N_2^L + N_3^L)$ is constant. If we consider the first layer of solvent molecules as constituting the local (cybotactic) region, the constancy of the total number of solvent molecules is valid when the molecules have the same size.[21] With this assumption, the number of independent composition variables in the expression for G reduces to two. Thus, taking N_1^L and N_2^L as two independent variables, we get the following two conditions for equilibrium solvation

$$kT \ln K_{13} = kT \ln[(N_1^L N_3)/(N_1 N_3^L)] = [\epsilon_{s3}^L - \epsilon_{s1}^L] + [N_1\epsilon_{11} - N_1^L\epsilon_{11}^L - N_3\epsilon_{33} + N_3^L\epsilon_{33}^L + (N_1^L - N_3^L)\epsilon_{31}^L - (N_1 - N_3)\epsilon_{31} + N_2\epsilon_{12} - N_2^L\epsilon_{12}^L - N_2\epsilon_{13} + N_2^L\epsilon_{23}^L + (\epsilon_{11}^L - \epsilon_{33}^L)/2 - (\epsilon_{11} - \epsilon_{33})/2] \quad (6)$$

and

$$kT \ln K_{23} = kT \ln[(N_2^L N_3)/(N_2 N_3^L)] = [\epsilon_{s3}^L - \epsilon_{s2}^L] + [N_2\epsilon_{11} - N_2^L\epsilon_{22}^L - N_3\epsilon_{23} + N_3^L\epsilon_{23}^L + (N_2^L - N_3^L)\epsilon_{32}^L - (N_2 - N_3)\epsilon_{32} + N_1\epsilon_{12} - N_2^L\epsilon_{12}^L - N_1\epsilon_{31} + N_1^L\epsilon_{31}^L + (\epsilon_{22}^L - \epsilon_{33}^L)/2 - (\epsilon_{22} - \epsilon_{33})/2] \quad (7)$$

The term K_{ij}, defined as $[(N_i^L N_j)/(N_i N_j^L)] = [(x_i^L x_j)/(x_i x_j^L)]$, may be looked upon as the equilibrium constant for the following solvent exchange equilibrium.

$$\bar{i} + j = i + \bar{j} \quad (8)$$

where $\bar{i}$ and $\bar{j}$ represent component solvent molecules in the local (cybotactic) region, while i and j represent those in the bulk. Equations 6 and 7 indicate that the value of K_{ij} is dependent on solute−solvent interaction and solvent−solvent interaction or solvent nonideality effect (terms in the first and second square brackets, respectively, in the right-hand side of eqs 6 and 7). Moreover, the solvent nonideality effect is dependent on the composition of the solvent mixture. When all of the ϵ-values are equal and $\epsilon_{ij}^L = \epsilon_{ij}$, which is equivalent to ideality of the solvent behavior, the terms in the second square bracket of eqs 6 and 7 vanish. Similar expressions for the equilibrium constant for the solvent exchange equilibrium have been derived previously for binary solvation.[21] The value of $K_{ij} \neq 1$ indicates that $x_i^L \neq x_i$, meaning that the composition of the solvent mixture in the local region is different from that in the bulk.

The maximum transition energy per mole, E_{123}, under these conditions, may be written as[26]

$$E_{123} = \sum N_i^L E_i \Big/ \sum N_i^L \quad (9)$$

In eq 9, $\sum N_i^L$ represents the total number of solvent molecules in the local region and, for solvent molecules having almost equal size, may be assumed to be constant. Thus, defining the local mole fraction as $x_i^L = N_i^L/\sum N_i^L$ (i = 1, 2, 3), we have

$$E_{123} = x_1^L E_1 + x_2^L E_2 + x_3^L E_3 \tag{10}$$

The value of x_i^L is, in general, different from that of x_i. This is because of differential solute−solvent interaction and solvent−solvent interaction as can be seen from eqs 6 and 7. Equation 10 is an extension of the similar equation applied for binary solvent mixture.[10,14,15,21]

To calculate the excess or deficiency of a solvent component in the cybotactic region over that in the bulk, we proceed as follows: From eqs 2 and 10. we write

$$\Delta = E_{123} - E_{123}(\text{ideal}) = \sum (x_i^L - x_i)E_i \tag{11}$$

Defining a quantity $\delta_i = (x_i^L - x_i)$, which is a measure of the excess or deficit of the i-solvent in the local region compared to that in the bulk, and noting that $\sum \delta_i = 0$, we have

$$\Delta = \delta_1(E_1 - E_3) + \delta_2(E_2 - E_3) \tag{12}$$

The component solvents of the ternary mixture in the present investigation have been chosen such that $E_1 > E_2 > E_3$. The overall sign of Δ thus depends on the signs of δ_1 and δ_2. Note that, unlike the case of binary solvation, the apparent deviation from ideality, $\Delta = 0$, does not necessarily mean the equality of local and bulk mole fractions ($\delta_i = 0$). Rather, the local compositions of all the components differ from that in the bulk in such a way that the value of the parameter E_{123} calculated according to eq 10 equals the ideal value. To calculate δ_1 and δ_2, we need another equation between δ_1 and δ_2. From the definition of K_{12}, it follows that $K_{12} = [(x_1 + \delta_1)x_2]/[x_1(x_2 + \delta_2)]$, which on rearrangement gives the following equation

$$(\delta_1/x_1) - (\delta_2 K_{12})/x_2 = (K_{12} - 1) \tag{13}$$

Thus, knowledge of the equilibrium constant for solvent exchange equilibrium, K_{12} (or, in general, K_{ij}), would lead to the evaluation of individual δ values. Values of K_{ij} cannot, however, be obtained from studies of solvation in a ternary solvent mixture. In our studies with binary solvent mixtures, it has been noted that electron spectroscopic studies provide a method for the estimation of K_{12}.[15] It has also been found that K_{12} values for binary solvent mixtures are smooth functions of the ratio of the mole fractions of the solvent components, x_1/x_2. Figure 3 shows the representative plots indicating composition dependence of K_{12} for binary mixtures. We have assumed that the preferential solvation parameter K_{12} (which is a measure of excess solute properties) obtained in binary solvent mixtures is transferable to ternary solvation for the same solute. A similar procedure for explaining excess solvent properties in a ternary mixture has been reported in the literature.[29−31] In our present work, we have assumed that the value of K_{12} in a ternary solvent mixture depends similarly on x_1/x_2 to that observed for binary solvation of the solute involving solvents 1 and 2. Thus, in our calculation for a particular ternary solvent composition (x_1, x_2, x_3), we have taken the value of K_{12} as obtained from the binary solvation of the solute for the same (x_1/x_2) ratio. For example, the value of K_{12} for the solute in the methanol (1) + water (2) binary mixture at a particular x_1/x_2 ratio, as calculated from the literature data,[10] has been used for the methanol (1) + water (2) + acetone (3) ternary mixture for the same x_1/x_2 ratio. Similarly, data for acetone + benzene[35] and methanol + chloroform[10] have been used for evaluating δ minus values for methanol + acetone + benzene and methanol + chloroform + benzene, respectively. Values of δ_1 and δ_2 were then calculated using eqs 12 and 13. The values have been listed in Tables 1−3.

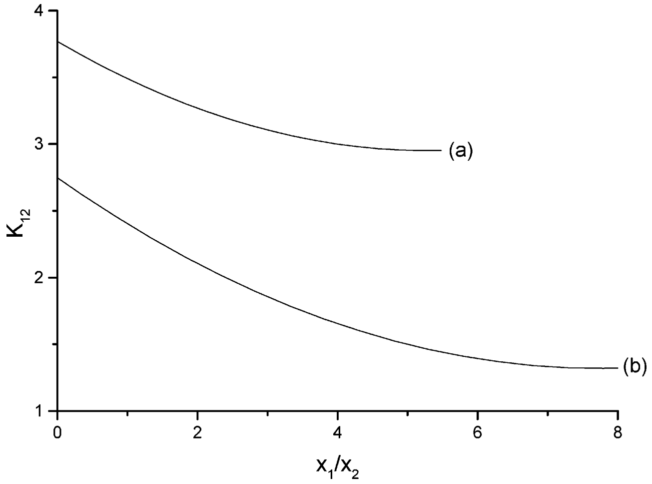


Figure 3. Experimental values of K_{12} as a function of x_1/x_2 for (a) methanol (1) + water (2) and (b) acetone (1) + benzene (2) mixed binary solvents for the indicator solute.

For methanol (1) + acetone (2) + benzene (3), the solvent sign of δ_1 is positive, while that of δ_2 or δ_3 is negative. A positive value of δ indicates that the solvent component 1 is in excess in the local region relative to the average composition. Thus, methanol is preferred in the local region. This is intelligible in terms of the high hydrogen bonding ability of methanol to the phenolate ion in the solute.[24] The positive value of δ_1 for the methanol (1) + chloroform (2) + benzene (3) mixture can be similarly explained. But, in this case, the value of δ_2 is positive. The different result obtained when chloroform replaces acetone in the ternary mixture is not very clearly understood. It is known that methanol and acetone form 1:1 hydrogen bonds,[29] and this solvent−solvent interaction may modify the preference of acetone (compared to that of chloroform) in a mixture containing methanol and benzene. The values of δ_1 are negative for the water (1) + methanol (2) + acetone (3) system, while the δ_2 values are positive, meaning that methanol is preferred in the local region of the solute whereas water molecules are deficient in that region. It can be mentioned in this context that electronic spectral studies of the dye in binary methanol + water mixed solvent indicates preferential solvation of the dye by methanol.[10] This can be rationalized in terms of self-association of the water molecules in the mixture.[12,36] Values of δ_3 for the ternary mixture are positive when the ratio $x_3/x_1 \leq 1.5$ and negative when the ratio exceeds 1.5. Thus, the signs of δ_3 and δ_1 are opposite when $x_3/x_1 \geq 1.5$, which is tantamount to saying that acetone is relatively richer than water in the local region than in the bulk acetone + water mixture in this region. It is interesting to note that solvation studies of the dye in an acetone + water binary mixed solvent indicate similar solvation behavior.[10,36] Thus, the characteristics of binary solvation are also retained in the case of ternary solvation of the same solute.

Conclusions

Information regarding the cybotactic zone around a solute in a ternary solvent mixture can be obtained by monitoring the electronic CT absorption band of the solute. The local composition of solvents in the local (cybotactic) region differs from that in the bulk and originates from solvent–solvent and differential solute–solvent interactions. A method has been discussed for the calculation of the excess or deficit of a solvent component in the local region relative to the average bulk composition using information obtained from binary solvation of the solute.

Acknowledgment. A gift of the betaine dye from Professor Ch. Reichardt, Marburg, Germany is gratefully acknowledged.

References and Notes

(1) Aznarez, S.; Katz, M.; Arancibia, E. L. *J. Solution Chem.* **2002**, *31*, 639.
(2) Segura, H.; Wisniak, J.; Galindo, G.; Reich, R. *Phys. Chem. Liq.* **2002**, *40*, 67.
(3) Acosta, J.; Arce, A.; Rodil, E.; Soto, A. *Fluid Phase Equilib*. **2002**, *203*, 83.
(4) Lotfollahi, M. N.; Modarress, H. *J. Chem. Phys.* **2002**, *116*, 2487.
(5) Garcia, B.; Alcalde, R.; Aparicio, S.; Leal, J. M.; Matos, J. S. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2866.
(6) Maurizio, C.; Vincenzo, B.; Benedetta, M.; Jacopo, T. *Chem. Phys. Lett.* **1998,** *286*, 253.
(7) Papazyan, A.; Warshel, A. *J. Chem. Phys.* **1997**, *107*, 7975.
(8) Qiu, D.; Shenkin, P. S.; Hollinger, F. P.; Still, W. C. *J. Phys. Chem.* **1997**, *101*, 3005.
(9) Tongraar, A.; Liedl, K. R.; Rode, B. M. *Chem. Phys. Lett.* **1998**, *286*, 56.
(10) Dawber, J. G.; Ward, J.; Williams, R. A. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 713.
(11) Chatterjee, P.; Bagchi, S. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1785.
(12) Chatterjee, P.; Laha, A. K.; Bagchi, S. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1675.
(13) Covington, A. K.; Dunn, M. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 2835.
(14) Suppan, P. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 495.
(15) Laha, A. K.; Das, P. K.; Bagchi, S. *J. Phys. Chem. A* **2002**, *106*, 3230.
(16) Mancini, P. M. E.; Adam, C.; Perez, A.; Vottero, L. R. *J. Phys. Org Chem.* **2000**, *13*, 221.
(17) Marcus, Y. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1465.
(18) Ben-Naim, A. *J. Phys. Chem.* **1989**, *93*, 3809.
(19) Covington, A. K.; Newman, K. E. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1393.
(20) Chandra, A.; Bagchi, B. *J. Chem. Phys.* **1991**, *94*, 8386.
(21) Banerjee, D.; Laha, A. K.; Bagchi, S. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 631.
(22) Itskovitch, E. M.; Ulstrup, J.; Vorotyntsev, M. A. In *The Chemical Physics of Solvation Part B*; Dogonadze, R. R., Kalman, E., Kornyshev, A. A., Ulstrup, J., Eds.; Elsevier: Amsterdam, 1986.
(23) Dimroth, K.; Reichardt, C. *Z. Anal. Chem.* **1966**, *215*, 344.
(24) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319, and the references therein.
(25) Ray, N.; Pramanik, R. K.; Das, P. K.; Bagchi, S. *Chem. Phys. Lett,* **2001**, *341*, 255.
(26) Ray, N.; Bagchi, S. *Chem. Phys. Lett.* **2002**, *364*, 621.
(27) Weissberger, A. *Technique of Organic Chemistry*; Interscience: New York, 1955; Vol. 7.
(28) Marcus, Y. *Ion Solvation*; John Wiley and Sons Ltd.: Chichester, 1985.
(29) Iglesias, M.; Orge, B.; Pineiro Cominges, M. M.; Cominges, B. E. D.; Marino, G.; Tojo, J. *J. Chem. Eng. Data* **1998**, *43*, 776.
(30) Venkatesu, P.; Prabhakara Rao, M. V. *J. Chem. Thermodyn.* **1998**, *30*, 207.
(31) Cibulka, I. *Collect. Czech. Chem. Commun.* **1982**, *47*, 1414.
(32) Acree, W. E., Jr.; McCarger, J. W.; Zvaigzne, A.; Teng, I.-L. *Phys. Chem. Liq.* **1991**, *23*, 27.
(33) Deng, T.; Childress, S. D.; Fina, K. M. D.; Acree, W. E., Jr. *Chem. Eng. Commun.* **1999**, *172*, 217.
(34) Marcus, Y. *J. Solution Chem.* **1991**, *20*, 929.
(35) Laha, A. K.; Banerjee, D.; Bagchi, S. *Indian J. Chem.* **1995**, *34A*, 335.
(36) Pramanik, R. K.; Bagchi, S. *Indian J. Chem.* **2002**, *41A*, 1580.